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(54) **Image-receiving sheet for thermal transfer printing with an intermediate layer**

Bildempfangsschicht für thermischen Übertragungsdruck mit einer Zwischenschicht

Feuille réceptrice pour l'impression thermique par transfert avec une couche intermédiaire

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(56) References cited:  
**EP-A- 0 454 428**                      **EP-A- 0 495 617**  
**EP-A- 0 544 283**                      **EP-A- 0 545 317**  
**US-A- 5 135 905**

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**EP 1 020 299 B1**

**Description**

[0001] The present invention relates to a thermal transfer image-receiving sheet. More particularly, it relates to a thermal transfer image-receiving sheet having a dye-receptive layer of which the texture is similar to that of the so-called "plain paper."

[0002] A thermal transfer sheet comprising a substrate sheet and a dye layer provided on one surface of the substrate sheet has hitherto been used in an output print for computers and word processors by a thermal sublimation dye transfer system. This thermal transfer sheet comprises a heat-resisting substrate sheet and a dye layer formed by coating an ink comprising a mixture of a binder with a sublimable dye on the substrate sheet and drying the resultant coating. Heat is applied to the thermal transfer sheet from the back surface thereof to transfer a number of color dots of three or four colors to a material on which an image is to be transferred, thereby forming a full color image. Since the colorant used is a dye, the image thus formed has excellent sharpness and transparency and high reproduction and gradation of intermediate colors, which enables a high-quality image comparable to the conventional full color photographic image to be formed.

[0003] Such a high-quality image, however, cannot be formed on a transfer material undyeable with a dye, such as plain paper. In order to solve this problem, a thermal transfer image-receiving sheet comprising a substrate sheet and a dye-receptive layer previously formed on the substrate sheet has been used in the art.

[0004] EP-A-0 545 317 describes in a first aspect a thermal transfer image-receiving sheet comprising a substrate and, formed on one surface of the substrate sheet, a resin layer comprising at least a dye-receiving layer.

[0005] Conventional thermal transfer image-receiving sheets are generally thick and have a dye-receptive layer of which the surface has a texture close to the so-called "photographic paper" rich in gloss, so that in some sense they can be said to give an impression of high grade.

[0006] However, in the so-called "applications in office," the gloss of the surface of the dye-receptive layer and the hard texture of the sheet per se give a poor image to users. In order to overcome this problem, a thermal transfer image-receiving sheet, particularly one which has a surface having a texture close to plain paper and can be handled like copying paper, has been desired in the art.

[0007] The present invention has been made under these circumstances, and an object of the present invention is to provide a thermal transfer image-receiving sheet, particularly one which particularly has a surface having a texture close to plain paper and can be handled like copying paper.

[0008] An image-receiving sheet using a conventional paper substrate sheet with an image being formed thereon is comparable to a print obtained by the conventional printing in texture, such as surface gloss and thickness, and, unlike an image-receiving sheet using the conventional synthetic paper as the substrate sheet, can be bent, and a plurality of sheets thereof may be put on top of one another for bookbinding or filing, which renders the thermal transfer image-receiving sheet using paper as the substrate sheet suitable for various applications. Further, since plain paper is more inexpensive than synthetic paper, the image-receiving sheet can be produced at a lower cost. In such an image-receiving sheet, in order to compensate for the cushioning property of the substrate sheet, it is generally preferred to provide as an interposing layer a layer having a high cushioning property, for example, an expanded layer (foamed layer) comprising a resin and an expanding agent (foaming agent).

[0009] The present invention provides a thermal transfer image-receiving sheet which has texture such as gloss and surface geometry comparable to paper, high printing sensitivity and causes neither dropout nor uneven density.

[0010] In order to solve the above problems, the present invention provides a thermal transfer image-receiving sheet comprising a substrate sheet of paper composed mainly of pulp and, provided on said substrate sheet in the following order, an expanded layer, an intermediate layer and a receptive layer, said intermediate layer having been formed by coating an aqueous coating solution.

[0011] In the thermal transfer image-receiving sheet according to the present invention, since the intermediate layer is formed by using an aqueous coating solution, it can be formed without breaking the cells of the expanded layer.

[0012] Further, since the intermediate layer and the receptive layer can be formed without breaking the surface geometry of the expanded layer, the geometry of a finely uneven surface of the expanded layer, as such, can be imparted to the surface of the receptive layer.

**The Invention**

[0013] Preferred embodiments of the thermal transfer image-receiving sheet according to the present invention will now be described in detail.

[0014] Paper composed mainly of pulp, which is commonly used in the art, may be used as the substrate sheet. Examples of the paper composed mainly of pulp include wood free paper, art paper, lightweight coated paper, slightly coated paper, coated paper, cast coated paper, paper impregnated with a synthetic resin or an emulsion, paper impregnated with a synthetic rubber latex, paper with a synthetic resin being internally incorporated therein and thermal

transfer paper. Among them, wood free paper, lightweight coated paper, slightly coated paper, coated paper and thermal transfer paper are preferred. The coated paper and the like may be prepared by coating base paper with a resin such as an SBR latex containing calcium carbonate, talc or the like. This type of resin layer cannot be sufficiently prevent the penetration of the coating solution for an expanded layer (foamed layer). Although some of the resin-impregnated paper, cast coated paper and the like have water resistance imparted by the impregnation or coating treatment, they are undesirable from the viewpoint of texture and cost.

[0015] When paper of the same type as used for proof reading in gravure printing, offset printing, screen printing and other various types of printing is used as the substrate sheet, trial printing may be directly carried out using the image-receiving sheet of the present invention without proof.

[0016] Among others, offset printing paper and the like are designed to be dried at about 200°C, so that they are relatively resistant to heat and less likely to cause curling derived from heat wrinkle or heat shrinkage in the course of heating of the expandable layer which will be described later. The thermal transfer paper too is less likely to cause curling derived from heat wrinkle and heat shrinkage in the course of heating of the expandable layer because it is designed to be heated by means of a thermal head when used.

[0017] The thickness of the substrate sheet used is in the range of from 40 to 250  $\mu\text{m}$ , preferably in the range of from 60 to 200  $\mu\text{m}$ . When it is contemplated for the resultant thermal transfer image-receiving sheet to have a texture like plain paper, the thickness of the thermal transfer image-receiving sheet is desirably in the range of from about 80 to 200  $\mu\text{m}$ . In this case, the thickness of the substrate sheet is a value obtained by subtracting the total thickness (about 30 to 80  $\mu\text{m}$ ) of the layers formed on the substrate sheet, such as the undercoat layer, expanded layer, intermediate layer and receptive layer, from the thickness of the thermal transfer image-receiving sheet. When the substrate sheet used has a relatively small thickness of not more than 90  $\mu\text{m}$ , it is likely to wrinkle due to absorption of water. In such a case, the effect of providing an undercoat layer is significant.

[0018] The colorant-receptive layer comprises a varnish composed mainly of a resin having a high dyability with a colorant and, optionally added to the varnish, various additives such as a release agent. Examples of the dyable resin include polyolefin resins, such as polypropylene, halogenated resins, such as polyvinyl chloride and polyvinylidene chloride, vinyl resins, such as polyvinyl acetate and polyacrylic esters, and copolymers thereof, polyester resins, such as polyethylene terephthalate and polybutylene terephthalate, polystyrene resins, polyamide resins, copolymer resins comprising olefins, such as ethylene or propylene, and other vinyl monomers, ionomers and cellulose derivatives. They may be used alone or in the form of a mixture of two or more. Among them, polyester resins and vinyl resins are particularly preferred. Further, any composite of the above resins may also be used.

[0019] It is also possible to incorporate a release agent into the colorant-receptive layer for the purpose of preventing the colorant-receptive layer being fused to a thermal transfer sheet at the time of formation of an image. silicone oils, phosphoric ester plasticizers and fluorocompounds may be used as the release agent. Among them, silicone oils are preferred. Preferred examples of the silicone oils include modified silicone oils such as epoxy-modified, alkyl-modified, amino-modified, carboxyl-modified, alcohol-modified, fluorine-modified, alkylarylalkyl-polyether-modified, epoxy-polyether-modified and polyether-modified silicone oils. Among others, a product of a reaction of a vinyl-modified silicone oil with a hydrogen-modified silicone oil provides good results.

[0020] The amount of the release agent added is preferably in the range of from 0.2 to 30 parts by weight based on the resin for forming the receptive layer.

[0021] The colorant-receptive layer and other layers described below may be formed by roll coating, bar coating, gravure coating, gravure reverse coating and other conventional coating methods. The coverage of the colorant-receptive layer is preferably in the range of from 1.0 to 10  $\text{g}/\text{m}^2$  (on a solid basis; the coverage in the present invention being hereinafter on a solid basis unless otherwise specified).

[0022] In the present invention, an undercoat layer may be formed on the substrate sheet. By virtue of the provision of the undercoat layer, even when a coating solution for an expanded layer is coated on the substrate sheet, the coating solution does not penetrate into the substrate sheet, so that an expandable layer having a desired thickness can be formed. Further, the expansion ratio in the expansion of the expandable layer by heating can be increased, which contributes to an improvement in cushioning property of the whole image-receiving sheet and, at the same time, is cost-effective because the amount of the coating solution necessary for the formation of an expanded layer having a desired thickness can be reduced.

[0023] Resins usable as the undercoat layer include acrylic resins, polyurethane resins, polyester resins and polyolefin resins and modification products of the above resins.

[0024] In the present invention, paper is used as the substrate sheet. Therefore, when an aqueous coating solution for an undercoat layer is coated directly on the paper as the substrate sheet, a wrinkle or waviness occurs due to uneven water absorption of the surface of the substrate sheet, which often has an adverse effect of the texture or print quality. This tendency is significant particularly when the substrate sheet used has a small thickness of not more than 100  $\mu\text{m}$ .

[0025] For this reason, the coating solution for an undercoat layer is preferably not aqueous but a coating solution

in the form of a solution or a dispersion of the resin in an organic solvent.

[0026] Organic solvents usable for this purpose include toluene, methyl ethyl ketone, isopropanol, ethyl acetate, butanol and other general industrial organic solvents.

[0027] Further, extenders, such as talc, calcium carbonate, titanium oxide and barium sulfate, may be added to improve the coatability of the coating solution for an undercoat layer, improve the adhesion of the undercoat layer to the substrate sheet and the expanded layer (particularly when an aqueous expanding agent is used in the formation of the expanded layer) or impart whiteness.

[0028] The coverage of the undercoat layer is preferably in the range of from 1 to 20 g/m<sup>2</sup>. when it is less than 1 g/m<sup>2</sup>, no contemplated effect as the undercoat layer can be attained. On the other hand, when it exceeds 20 g/m<sup>2</sup>, the effect is saturated and the large coverage effects the texture of the substrate to cause a texture like a synthetic resin sheet. This is also cost-ineffective.

[0029] An expanded layer comprising a resin and an expanding agent (foaming agent) is formed on the undercoat layer. The cushioning property of the expanded layer is so high that a thermal transfer image-receiving sheet having a high printing sensitivity can be provided even when paper is used as the substrate sheet.

[0030] Conventional resins, such as urethane resins, acrylic resins, methacrylic resins and modified olefin resins, or blends of the above resins may be used as a resin for constituting the expanded layer. A solution and/or a dispersion of the above resin in an organic solvent or water is coated to form an expandable layer. The coating solution for an expanded layer is preferably an aqueous coating solution which does not have any effect on the expanding agent, and examples of the coating solution include coating solutions using water-soluble or water-dispersible resins, SBR latex, suspensions, such as a urethane suspension, a polyester suspension, a suspension of vinyl acetate or a copolymer thereof, a suspension of acryl or a copolymer of acryl, such as acrylstyrene, and a vinyl chloride suspension or dispersions thereof. When a microsphere described below is used as the expanding agent, it is preferred to use a suspension of vinyl acetate or a copolymer thereof, or a suspension of acryl or a copolymer of acryl, such as acrylstyrene, among the above resins.

[0031] Since the glass transition point, flexibility and film formability can be easily controlled as desired by varying the kind and ratio of monomers to be copolymerized, these resins are advantageous in that desired properties can be obtained without the addition of any plasticizer or film forming aid and the resultant film is less likely to cause a change in color during storage under various environments and less likely to cause a change in properties with the lapse of time.

[0032] Further, among the above resins, SBR latex is not generally preferably used because it has a low glass transition point and is likely to cause blocking and the resultant film is likely to cause yellowing after the formation thereof during storage.

[0033] The urethane suspension is not preferably used because in many cases it contains solvents, such as NMP and DMF, which are likely to have an adverse effect on the expanding agent.

[0034] Further, the suspension or dispersion of a polyester and the vinyl chloride suspension are not preferably used because they generally have a high glass transition point and hence deteriorate the expandability of the microsphere. Although some of them are flexible, they too are not preferably used because a plasticizer is added to impart the flexibility.

[0035] The expanding property of the expanding agent is greatly influenced by the hardness of the resin. In order to attain a desired expansion ratio, the resin preferably has a glass transition point in the range of from -30 to 20°C or a minimum film forming temperature of 20°C or below. When the glass transition point is above 20°C, the flexibility is so low that the expanding property of the expanding agent is lowered. On the other hand, when the glass transition point is below -30°C, unfavorable phenomena often occur such as blocking (between the expanded layer and the back surface of the substrate sheet at the time of taking up the substrate sheet after the formation of the expanded layer) due to the tackiness of the resin and unsatisfactory cutting of the thermal transfer image-receiving sheet (occurrence of phenomena such as a deterioration in appearance of the thermal transfer image-receiving sheet due to sticking of the resin of the expanded layer to the cutting edge of a cutter or a deviation in cutting dimension at the time of cutting of the image-receiving sheet). When the minimum film forming temperature is above 20°C, a failure to form a film occurs during coating or drying, which results in occurrence of unfavorable phenomena such as surface cracking.

[0036] Examples of the expanding agent include conventional expanding agents, such as decomposable expanding agents, which decompose on heating to evolve oxygen, carbon dioxide gas, nitrogen or other gases, such as dinitropentamethylenetetramine, diazoaminobenzene, azobisisobutyronitrile or azodicarbonamide, or microspheres prepared by emicrocapsulating a low-boiling liquid, such as butane or pentane, in a resin, such as polyvinylidene chloride or polyacrylonitrile. Among them, a microsphere prepared by emicrocapsulating a low-boiling liquid, such as butane or pentane, in a resin, such as polyvinylidene chloride or polyacrylonitrile, is preferred. These expanding agents expand on heating after the formation of an expandable layer, and the resultant expanded layer has high cushioning property and heat insulating properties.

[0037] The amount of the expanding agent used is preferably in the range of from 1 to 150 parts by weight based on 100 parts by weight of the resin for forming the expanded layer. When it is less than 1 part by weight, the cushioning

property of the expanded layer is so low that the effect of forming the expanded layer cannot be attained. On the other hand, when it exceeds 150 parts by weight, the percentage hollow after the expansion becomes so high that the mechanical strength of the expanded layer is lowered, so that the image-receiving sheet cannot withstand ordinary handling. Further, the surface of the expanded layer loses its smoothness, which is likely to have an adverse effect on the appearance and print quality.

[0038] The thickness of the whole expanded layer is preferably in the range of from 30 to 100  $\mu\text{m}$ . When it is less than 30  $\mu\text{m}$ , the cushioning property and the heat insulating property become unsatisfactory. On the other hand, when it exceeds 100  $\mu\text{m}$ , the effect of the expanded layer cannot be improved and the strength is unfavorably lowered.

[0039] The expanding agent is preferably such that the volume average particle diameter before expansion is in the range of from about 5 to 15  $\mu\text{m}$  and the particle diameter after expansion is in the range of from 20 to 50  $\mu\text{m}$ . When the volume average particle diameter before expansion is less than 5  $\mu\text{m}$  and the particle diameter after expansion is less than 20  $\mu\text{m}$ , the cushioning effect is low. On the other hand, when the volume average particle diameter before expansion exceeds 15  $\mu\text{m}$  and the particle diameter after expansion is in the range of from 20 to 50  $\mu\text{m}$  or more, the surface of the expanded layer becomes uneven, which unfavorably has an adverse effect on the quality of the formed image.

[0040] The expanding agent is particularly preferably such a low temperature expanding microsphere that the softening temperature of the wall and the expansion initiation temperature are each 100°C or below and the optimal expansion temperature (the temperature at which the highest expansion ratio is obtained with the heating time being 1 min) is 140°C or below. In this case, the expansion is preferably carried out at as low a heating temperature as possible. The use of a microsphere having a low expansion temperature prevents the substrate sheet from wrinkling or curling on heating at the time of expansion.

[0041] The microsphere having a low expansion temperature can be prepared by regulating the amount of the thermoplastic resin incorporated for forming the wall of the microcapsule, such as polyvinylidene chloride or polyacrylonitrile. The volume average particle diameter of the microsphere is in the range of from 5 to 15  $\mu\text{m}$ .

[0042] The expanded layer formed using the above microsphere has advantages including that cells formed by the expansion are closed cells, the expansion can be carried out by simply heating the expandable layer and the thickness of the expanded layer can be easily controlled as desired by varying the amount of the microsphere incorporated.

[0043] The microsphere, however, is less resistant to organic solvents, and the use of a coating solution containing an organic solvent for the formation of an expanded layer causes the wall of the microsphere to be attacked by the organic solvent, which lowers the expanding property. For this reason, when the microsphere of the type described above is used, it is preferred to use an aqueous coating solution not containing such an organic solvent as will attack the wall, for example, ketones, such as acetone and methyl ethyl ketone, esters, such as ethyl acetate, and lower alcohols, such as methanol and ethanol.

[0044] Therefore, the use of an aqueous coating solution, specifically a coating solution using a water-soluble or water-dispersible resin, a suspension of a resin, still preferably an acrylstyrene suspension or a modified vinyl acetate suspension is preferred.

[0045] Further, even when an expandable layer is formed using an aqueous coating solution, the addition of a high-boiling, high-polar solvent, for example, a cosolvent or film forming aid or a plasticizer, such as NMP, DMF or cellosolve, to the coating solution affects the microsphere. Therefore, the composition of the aqueous resin used and the amount of the high-boiling solvent added should be properly selected by confirming that they do not have an adverse effect on the microcapsule.

[0046] In the present invention, the intermediate layer is formed by using an aqueous coating solution. The aqueous coating solution refers to an aqueous solution of a water-soluble resin, a dispersion of a resin or a suspension of a resin. Preferably, it does not contain organic solvents, for example, ketones, such as acetone and methyl ethyl ketone, esters, such as ethyl acetate, lower alcohols, such as methanol and ethanol, and high-boiling, high-polar solvents, such as NMP, DMF and cellosolve. When the above organic solvent is contained in the coating solution, it is necessary to select such an organic solvent as will not affect the microsphere in the expanded layer or to regulate the organic solvent content.

[0047] The resin particle diameter is not more than 0.01  $\mu\text{m}$  for the aqueous solution of a water-soluble resin, in the range of from about 0.01 to 0.1  $\mu\text{m}$  of the dispersion of a resin and more than 0.1  $\mu\text{m}$  for the suspension. Among the above coating solutions, the suspension is preferred for the following reasons.

[0048] In the water-soluble resin, the proportion of the hydrophilic portion in the polymer chain is so high that the formed coating has poor water resistance. Further, if a polymer having a high molecular weight is used as the water-soluble resin, the resultant aqueous solution has a high viscosity. For this reason, a resin having a low molecular weight should be used, so that the necessary coverage cannot be often obtained. Furthermore, since a crosslinking reaction is necessary in the formation of a film, heat treatment and other steps should be additionally provided. Furthermore, a hydrophilic organic solvent is added as an assistant for rendering the resin aqueous, and such an assistant may have an adverse effect on the microsphere in the expanded layer depending upon the kind and the amount thereof.

**[0049]** In the case of the suspension, the molecular weight of the resin used does not affect the viscosity of the suspension, so that a resin having a high molecular weight can be used. This enables good coating properties to be obtained without crosslinking reaction and other treatments. Further, a coating solution having a solid content and a low viscosity can be prepared, which facilitates the coverage. Furthermore, there is little or no need to use any organic solvent as an assistant, so that an adverse effect of the organic solvent on the expanded layer can be avoided.

**[0050]** The dispersion has properties between the aqueous solution of a water-soluble resin and the suspension. For the above reasons, the use of the suspension is preferred. However, the water-soluble resin and the dispersion too can be usefully employed if the following precautions are taken.

**[0051]** Specifically, a solution, dispersion or suspension of a urethane resin, a vinyl acetate resin, an acrylic resin, a copolymer of the above resins or a blend of the above resins in water is used as a coating solution or an intermediate layer. The coating solution is coated on the expanded layer by various coating methods, and the resultant coating is then dried to form an intermediate layer. The intermediate layer (aqueous intermediate layer) composed mainly of the above water-soluble resin, water-dispersible resin or suspension resin can cover the surface of the expanded layer without attacking the cells, particularly microspheres in the expanded layer. Therefore, the expanded layer having high cushioning property and heat insulating property can remain unchanged.

**[0052]** In order to impart a texture like plain paper to the thermal transfer image-receiving sheet, proposals have hitherto been made such as a method wherein the surface of the receptive layer is heated and pressed with a matting metal roll to impart matte feeling and a method which comprises providing a plurality of resin layers including a receptive layer on a plastic substrate sheet, which has been previously matted, laminating the resin layer to paper and peeling off the plastic substrate sheet, thereby forming on paper a resin layer having a matte feeling. Both the above methods, however, have drawbacks such as complicated process steps and occurrence of excessive wastes. By contrast, in the case of the thermal transfer image-receiving sheet using the above aqueous intermediate layer, the intermediate layer and the receptive layer can be formed while utilizing the roughness derived from microspheres of the expanded layer, so that a thermal transfer image-receiving sheet having natural matte feeling can be prepared without providing any special step.

**[0053]** The uneven portions formed on the surface of the receptive layer due to the influence of the roughness of the surface of the expanded layer often leads to occurrence of dropouts or voids when an image is formed. In order to solve this problem, proposals have been made such as a method wherein a smoothening treatment is carried out by calendaring with heating and pressing and other methods, a method wherein a large amount of a resin is coated on the expanded layer to smoothen the surface of the expanded layer and a method which comprises forming on a releasable substrate sheet a receptive layer and an expanded layer in that order, laminating the resultant laminate onto a separately provided substrate sheet and peeling off the releasable substrate sheet alone to form an image-receiving sheet.

**[0054]** All the above methods, however, are not favorable because the number of process steps should be increased, a large amount of resin coating is necessary, or other members should be additionally used.

**[0055]** A good method for eliminating the problem associated with the uneven surface of the expanded layer is to provide on the expanded layer an intermediate layer comprising a flexible and elastic material. By virtue of the provision of the intermediate layer, a thermal transfer image-receiving sheet, which does not affect the print quality, can be provided even when the surface of the receptive layer is uneven.

**[0056]** The intermediate layer comprises a resin having excellent flexibility and elasticity. Specifically, among the above resins, those having a glass transition point in the range of from -30 to 20°C are preferred. The use of the resin having a glass transition point in the range of from -30 to 20°C enables an intermediate layer having a satisfactory flexibility to be formed, so that even though the surface of the receptive layer is uneven due to the influence of the roughness of the expanded layer, neither dropout nor uneven density occurs and a high-quality image can be provided.

**[0057]** When the glass transition temperature is below -30°C, the tackiness is so large that blocking (between the intermediate layer and the back surface of the substrate sheet) at the time of taking up the thermal transfer sheet or unfavorable phenomena at the time of cutting of the thermal transfer image-receiving sheet occurs. Further, the heat resistance is so poor that the surface of the image-receiving sheet is matted in the case of high-density printing to give a rough texture or a low reflection density. On the other hand, when the glass transition point is above 20°C, the flexibility becomes unsatisfactory, so that the effect of the cushioning property exerted by the expanded layer cannot be often attained.

**[0058]** Further, the use of a crosslinking resin as the resin for the intermediate layer is also preferred. The crosslinking resin causes a crosslinking reaction at the time of forming a coating, thereby forming a three-dimensional network structure which serves to improve the heat resistance and prevent the surface of the image-receiving sheet from being matted. Further, since the solvent resistance is also improved, even though the receptive layer is formed by a coating solution using an organic solvent, there is no fear of the intermediate layer and the expanded layer being attacked by the organic solvent. Furthermore, cells, particularly microspheres, in the expanded layer can be protected against heat at the time of drying of the intermediate layer or the receptive layer.

[0059] The use of a self-crosslinking resin among the crosslinking resins is preferred. The self-crosslinking resin is a resin which has in its polymer chain one or several kinds of heat-reactive functional groups which react with each other to form a crosslinked structure.

[0060] The reaction rate of the above self-crosslinking resin at a low temperature around room temperature is so low that the coating solution can be stably stored and hence is easy to handle and, further, does not deteriorate in the course of coating. After the coating, the crosslinked structure can be formed by heating and drying. Since the use of any curing agent, such as an isocyanate, is not required, the handleability is good. Furthermore, among the self-crosslinking resins, those which crosslink on heating, are preferred for simplification of equipment of reaction process.

[0061] The intermediate layer formed using a self-crosslinking resin neither loses its flexibility at a low temperature nor becomes liquid at a high temperature to exhibit rubber-like behavior, so that the resistance to heat and scratch is so high that neither matting of the surface of the receptive layer nor scratch occurs even in the case of high-density printing.

[0062] The intermediate layer or the expanded layer may further comprise calcium carbonate, talc, kaolin, titanium oxide, zinc oxide and other conventional inorganic pigments and brightening agents for the purpose of imparting shielding properties and whiteness and regulating the texture of the thermal transfer image-receiving sheet. The amount of these optional additives is preferably in the range of from 10 to 200 parts by weight based on 100 parts by weight of the resin (on a solid basis). When it is less than 10 parts by weight, the effect is unsatisfactory. On the other hand, when it exceeds 200 parts by weight, the dispersion stability is poor and the resin performance cannot often be attained.

[0063] The coverage of the intermediate layer is preferably in the range of from 1 to 20 g/m<sup>2</sup>. When the coverage is less than 1 g/m<sup>2</sup>, the function of protecting the cells cannot be sufficiently exhibited. On the other hand, when it exceeds 20 g/m<sup>2</sup>, the heating insulating property, cushioning property and other properties of the expanded layer cannot be exhibited.

[0064] When the substrate sheet according to the present invention is used, if a plurality of resin layers are formed on the substrate sheet on the side of the receptive layer with the substrate sheet, such as plain paper, being exposed as such on the side of the back surface, the thermal transfer image-receiving sheet is likely to curl due to environmental moisture and temperature. For this reason, it is preferred to provide a curl preventive layer composed mainly of a resin having a water retaining property, such as polyvinyl alcohol or polyethylene glycol, on the back surface of the substrate sheet.

[0065] Further, it is also possible to provide a back surface layer having lubricity in the image-receiving sheet on its surface remote from the colorant-receptive layer according to a conveying system for the thermal transfer image-receiving sheet in a printer used. In order to impart the lubricity to the back surface layer, an inorganic or organic filler is dispersed in the resin of the back surface layer. Examples of the resin used in the back surface layer having lubricity include conventional resins or a blend of the conventional resins.

[0066] Furthermore, a lubricating agent, such as a silicone oil, or a release agent may be added to the back surface layer. The coverage of the back surface layer is preferably in the range of from 0.05 to 3 g/m<sup>2</sup>.

[0067] Thermal transfer sheets usable in thermal transfer, which is carried out using the above thermal transfer image-receiving sheet, include, beside a sublimation dye transfer sheet used in the sublimation dye transfer recording system, a hot-melt thermal transfer sheet wherein a hot-melt ink layer comprising a hot-melt binder bearing a pigment is formed on the a substrate sheet by coating and the ink layer is transferred by heating to a material on which an image is to be formed.

[0068] Means for applying a thermal energy in the thermal transfer may be any conventional device. For example, an image can be formed by applying a thermal energy of about 5 to 100 mJ/mm<sup>2</sup> through the control of a recording time by means of a thermal printer (for example, a video printer VY-100 manufactured by Hitachi, Limited).

[0069] The present invention will now be described in more detail with reference to the following examples and comparative examples.

#### Example C1

[0070] A coated paper having a basis weight of 104.7 g/m<sup>2</sup> (Mitsubishi New V Matt Kote manufactured by Mitsubishi Paper Mills Limited) was provided as a substrate sheet, and a coating solution having the following composition for an undercoat layer was gravure-coated on the substrate sheet at a coverage of 5 g/m<sup>2</sup> (weight on a dry basis; the same shall apply hereinafter). The resultant coating was dried by a hot-air drier to form an undercoat layer.

[0071] Units for expressing the composition are parts by weight unless otherwise specified.

Coating solution for undercoat layer	
Polyester resin (V600 manufactured by Toyobo Co., Ltd.)	100 parts

(continued)

Coating solution for undercoat layer	
Methyl ethyl ketone/toluene = 1/1	400 parts

[0072] Then, a coating solution having the following composition for an expanded layer was gravure-coated on the undercoat layer at a coverage of 20 g/m<sup>2</sup>.

Thereafter, the resultant coating was dried and heated at 140°C for 1 min by a hot-air drier to expand the microsphere.

Coating solution for expanded layer	
EVA suspension (XB3647B manufactured by Tohpe Corporation)	100 parts
Microsphere (551WU20 manufactured by Expancel; expansion initiation temp. = 99-104°C)	20 parts
Water	20 parts

[0073] Then, a coating solution having the following composition for an intermediate layer was gravure-coated on the expanded layer at a coverage of 5 g/m<sup>2</sup>.

Thereafter, the resultant coating was dried by a hot-air drier.

Coating solution for intermediate layer	
Acrylic/styrene suspension (RX832A manufactured by Nippon Carbide Industries Co., Ltd.; glass transition point = 19°C)	100 parts
Water	20 parts

[0074] Then, a coating solution having the following composition for a receptive layer was gravure-coated on the intermediate layer at a coverage of 3 g/m<sup>2</sup>.

Thereafter, the resultant coating was dried by a hot-air drier.

Coating solution for receptive layer	
Vinyl chloride/vinyl acetate copolymer (#1000D manufactured by Denki Kagaku Kogyo K.K.)	100 parts
Amino-modified silicone (X22-349 manufactured by The Shin-Etsu Chemical Co., Ltd.)	3 parts
Epoxy-modified silicone (KF-393 manufactured by The Shin-Etsu Chemical Co., Ltd.)	3 parts
Methyl ethyl ketone/toluene = 1/1	400 parts

[0075] A coating solution having the following composition for a back surface layer was gravure-coated on the substrate sheet on its side remote from the receptive layer at a coverage of 0.05 g/m<sup>2</sup>. Thereafter, the resultant coating was dried by means of a cold-air dryer, thereby preparing a thermal transfer image-receiving sheet of Example C1.

Coating solution for back surface layer	
Polyvinyl alcohol (PVA124 manufactured by Kuraray Co., Ltd.)	2 parts
Water	100 parts

#### Example C2

[0076] A thermal transfer image-receiving sheet of Example C2 was prepared in the same manner as in Example C1, except that a coated paper having a basis weight of 127.9 g/m<sup>2</sup> (OK Coat manufactured by New Oji Paper Co., Ltd.) was provided as a substrate sheet, and the compositions of the undercoat layer, expanded layer and intermediate layer were varied as follows.



Coating solution for undercoat layer	
Acrylic resin (EM manufactured by Soken Chemical Engineering Co., Ltd.)	100 parts
Precipitated barium sulfate (#300 manufactured by Sakai Chemical Co., Ltd.)	30 parts
Toluene	400 parts

Coating solution for expanded layer	
Styrene/acrylic suspension (RX941A manufactured by Nippon Carbide Industries Co., Ltd.)	100 parts
Microsphere (F30VS manufactured by Matsumoto Yushi Kagaku K.K., Japan; expansion initiation temp. = 80°C)	10 parts
Water	20 parts

Coating solution for intermediate layer	
Acrylic suspension (completely self-crosslinking type; glass transition temp. = -5°C) (FX337C manufactured by Nippon Carbide Industries Co., Ltd.)	100 parts
Water	20 parts

Example C3

**[0077]** A thermal transfer image-receiving sheet of Example C3 was prepared in the same manner as in Example C1, except that a thermal transfer paper having a basis weight of 79.1 g/m<sup>2</sup> (TTR-T manufactured by Mitsubishi Paper Mills, Ltd.) was provided as a substrate sheet, and the compositions of the undercoat layer, expanded layer and intermediate layer were varied as follows.

Coating solution for undercoat layer	
Urethane resin (HL2371M30 manufactured by Mitsui Toatsu Chemicals, Inc.)	100 parts
Titanium oxide (TCA888 manufactured by Tohchem Products Corporation)	30 parts
Ethyl acetate	100 parts
Dimethylformamide	20 parts
Isopropanol	300 parts

Coating solution for expanded layer	
Acrylic suspension (AE312 manufactured by Japan Synthetic Chemicals, Inc.)	100 parts
Microsphere (F30SS manufactured by Matsumoto Yushi Kagaku K.K., Japan; expansion initiation temp. = 80°C)	15 parts
Water	20 parts

Coating solution for intermediate layer	
Acrylic ester suspension (glass transition temp. = -19°C) (RX669R manufactured by Nippon Carbide Industries Co., Ltd.)	100 parts

(continued)

Coating solution for intermediate layer	
Titanium oxide (TT-055 (A) manufactured by Ishihara Sangyo Kaisha Ltd.)	50 parts
Water	30 parts

Example C4

[0078] A thermal transfer image-receiving sheet of Example C4 was prepared in the same manner as in Example C1, except that a completely self-crosslinking type acrylic suspension (EX6074 manufactured by Nippon Carbide Industries Co., Ltd.; glass transition temp. = 7°C) was used instead of the resin for an intermediate layer of Example C1.

Example C5

[0079] A thermal transfer image-receiving sheet of Example C5 was prepared in the same manner as in Example C2, except that the composition of the undercoat layer in Example C2 was varied as follows. Further the formation of the back surface layer was omitted.

Coating solution for undercoat layer	
Acrylic suspension (AE932 manufactured by Japan Synthetic Chemicals, Inc.)	100 parts
Water	20 parts

Example C6

[0080] A thermal transfer image-receiving sheet of Example C6 was prepared in the same manner as in Example C1, except that an acrylic suspension (AE20 manufactured by Japan Synthetic Chemicals, Inc.; glass transition temp. = -45°C) was used instead of the resin for an intermediate layer of Example C4.

Comparative Example C1

[0081] A thermal transfer image-receiving sheet of Comparative Example C1 was prepared in the same manner as in Example C1, except that the formation of the intermediate layer was omitted.

Comparative Example C2

[0082] A thermal transfer image-receiving sheet of Comparative Example C2 was prepared in the same manner as in Example C2, except that the formation of the intermediate layer was omitted.

Comparative Example C3

[0083] A thermal transfer image-receiving sheet of Comparative Example C3 was prepared in the same manner as in Example C3, except that the formation of the undercoat layer and back surface layer was omitted.

Comparative Example C4

[0084] A thermal transfer image-receiving sheet of Comparative Example C4 was prepared in the same manner as in Example C1, except that the composition of the intermediate layer was varied as follows.

Coating solution for intermediate layer	
Acrylic resin (Dianal BR85 manufactured by Mitsubishi Rayon Co., Ltd.)	200 parts
Toluene	200 parts
Ethyl acetate	300 parts

[0085] The results of evaluation for the thermal transfer image-receiving sheets of Examples C1 to C6 and Comparative Examples C1 to C4 are given in Tables C1 and C2. The evaluation was carried out by the following methods.

1) Thickness of expanded layer

[0086] The section of the thermal transfer image-receiving sheet was observed using a photomicrograph thereof to measure the thickness of the expanded layer (unit:  $\mu\text{m}$ ).

2) Wrinkle and waviness of substrate sheet

[0087] The wrinkle and waviness of the substrate sheet were evaluated by visually inspecting the thermal transfer image-receiving sheet.

O: Good

$\Delta$ : Somewhat wrinkle and waviness observed

x: Significant wrinkle and waviness observed

3) Tackiness of cut end face

[0088] For each image-receiving sheet, 20 sheets were put on top of one another and cut with a table paper cutter, and the tackiness (stickiness) of the cut end face was evaluated by touch.

O: Not tacky

$\Delta$ : Somewhat tacky

x: Very tacky

4) Surface texture

[0089] The surface texture was evaluated by visually inspecting the thermal transfer image-receiving sheet.

O: Natural matte feeling like plain paper

$\Delta$ : Somewhat glossy

x: Highly glossy, and different in texture from plain paper.

5) Environmental curling

[0090] The thermal transfer image-receiving sheet was cut into a 10-cm square form. The cut sheets were allowed to stand on a floor with ① the surface of the receptive layer facing upward for one sheet and ② the surface of the receptive layer facing downward for another sheet in two types of environments, that is, an environment of a temperature of 20°C and a humidity of 30% for 2 hr and an environment of a temperature of 40°C and a humidity of 90% for 2 hr. Thereafter, the height from the floor was measured with respect to four corners of the thermal transfer image-receiving sheet, and the average of the measured values was calculated.

O: Not more than 10 mm in both environments for both sheets ① and ②

X: Not less than 10 mm in either or both environments for either or both sheets ① and ②

6) Quality of print

[0091] A solid image of 64/256 gradation for each of four colors of yellow, magenta, cyan and black was formed on the thermal transfer image-receiving sheet by using a sublimation dye transfer printer PHOTOMAKER manufactured by Seiko Instruments Inc. and a sublimation dye transfer sheet CH743, and the resultant print was evaluated by visual inspection.

O: Good quality with dropout and lack of uniformity being unobserved

$\Delta$ : Somewhat unsatisfactory

X: Remarkable dropout and lack of uniformity

## 7) Printing sensitivity

[0092] A solid image of 256/256 gradation for magenta was formed on the thermal transfer image-receiving sheet by using the above printer and transfer sheet, and the reflection density was measured with a Macbeth densitometer RD-918.

- : Reflection density of not less than 1.7  
 Δ: Reflection density of 1.5 to less than 1.7  
 X: Reflection density of less than 1.5

## 8) Matting

[0093] The surface of a print formed under the same conditions as those described above in connection with the measurement of the printing sensitivity was evaluated by visual inspection.

- : No matte feeling observed  
 Δ: Somewhat matte feeling observed  
 x: Significant matte feeling observed

Table C1

Samples	Thickness of expanded layer	Wrinkle etc.	Tackiness on end face	Surface texture
Ex. C1	70	○	○	○
Ex. C2	65	○	○	○
Ex. C3	80	○	○-Δ	○
Ex. C4	65	○	○	○
Ex. C5	65	Δ	○	○
Ex. C6	65	○	X	○
Comp. Ex. C1	50	○	○	Δ
Comp. Ex. C2	45	○	○	Δ
Comp. Ex. C3	70	○	○	○
Comp. Ex. C4	55	○	○	Δ

Table C2

Samples	Environmental curling	Quality of print	Printing sensitivity	Matting
Ex. C1	○	○	○	Δ
Ex. C2	○	○	○	○
Ex. C3	○	○	○	Δ
Ex. C4	○	○	○	○
Ex. C5	X	○	○	○
Ex. C6	○	○	Δ	Δ-X
Comp. Ex. C1	○	X	X	Δ-X
Comp. Ex. C2	○	X	X	Δ-X
Comp. Ex. C3	○	Δ-X	○	○
Comp. EX. C4	○	X	Δ	○

[0094] In the thermal transfer image-receiving sheet of the present invention, high cushioning property and heat

insulating properties of an expanded layer can remain unchanged by virtue of the function of an intermediate layer comprising an aqueous coating.

[0095] Further, the surface of the expanded layer is finely uneven due to the influence of an expanding agent, and the surface can be kept uneven. This enables a thermal transfer image-receiving sheet having a high image quality to be prepared while enjoying natural matte feeling.

# Claims

1. A thermal transfer image-receiving sheet comprising a substrate sheet of paper composed mainly of pulp and, provided on said substrate sheet in the following order, a foamed layer, an intermediate layer and a receptive layer, said intermediate layer having been formed by coating an aqueous coating solution.
2. The thermal transfer image-receiving sheet according to claim 1, wherein said aqueous coating solution is an aqueous solution of a water-soluble resin, a dispersion of a resin or a suspension of a resin.
3. The thermal transfer image-receiving sheet according to claim 1 or 2, wherein said resin constituting said intermediate layer has a glass transition temperature in the range of from -30 to 20°C.
4. The thermal transfer image-receiving sheet according to anyone of claims 1 to 3, wherein said resin constituting said intermediate layer is a crosslinking resin.
5. The thermal transfer image-receiving sheet according to anyone of claims 1 to 4, wherein an undercoat layer is provided between said substrate sheet and said foamed layer.

# Patentansprüche

1. Thermotransfer-Bildempfangsblatt, umfassend ein Substratblatt aus Papier, welches hauptsächlich aus Pulpe zusammengesetzt ist, und wobei auf dem Substratblatt in der nachfolgenden Reihenfolge eine geschäumte Schicht, eine Zwischenschicht und eine Empfangsschicht bereitgestellt sind, wobei die Zwischenschicht durch Beschichten einer wässrigen Beschichtungslösung gebildet ist.
2. Thermotransfer-Bildempfangsblatt nach Anspruch 1, wobei die wässrige Beschichtungslösung eine wässrige Lösung eines wasserlöslichen Harzes, einer Dispersion eines Harzes oder einer Suspension eines Harzes ist.
3. Thermotransfer-Bildempfangsblatt nach Anspruch 1 oder 2, wobei das Harz, welches die Zwischenschicht aufbaut, eine Glasübergangstemperatur in einem Bereich von -30 bis 20°C aufweist.
4. Thermotransfer-Bildempfangsblatt nach einem der Ansprüche 1 bis 3, wobei das Harz, welches die Zwischenschicht aufbaut, ein vernetztes Harz ist.
5. Thermotransfer-Bildempfangsblatt nach einem der Ansprüche 1 bis 4, wobei eine Unterschicht zwischen dem Substratblatt und der geschäumten Schicht bereitgestellt ist.

# Revendications

1. Feuille réceptrice d'image par transfert thermique comprenant une feuille substrat de papier se composant principalement de pâte et, prévues sur ladite feuille substrat dans l'ordre suivant, une couche alvéolaire, une couche intermédiaire et une couche réceptrice, ladite couche intermédiaire ayant été formée en déposant une solution de revêtement aqueuse.
2. Feuille réceptrice d'image par transfert thermique selon la revendication 1, dans laquelle ladite solution de revêtement aqueuse est une solution aqueuse d'une résine soluble dans l'eau, une dispersion d'une résine ou une suspension d'une résine.
3. Feuille réceptrice d'image par transfert thermique selon la revendication 1 ou 2, dans laquelle ladite résine cons-

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tituant ladite couche intermédiaire présente une température de transition vitreuse dans la plage de -30 à 20°C.

4. Feuille réceptrice d'image par transfert thermique selon l'une quelconque des revendications 1 à 3, dans laquelle ladite résine constituant ladite couche intermédiaire est une résine de réticulation.
5. Feuille réceptrice d'image par transfert thermique selon l'une quelconque des revendications 1 à 4, dans laquelle une sous-couche est prévue entre ladite feuille substrat et ladite couche alvéolaire.